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Electrostatic Analysis of Chiral Phase Separation in a Dipolar Monolayer Domain : Perturbation Analysis(Poster session 1, New Frontiers in Colloidal Physics : A Bridge between Micro- and Macroscopic Concepts in Soft Matter)

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Electrostatic Analysis of Chiral Phase Separation in a Dipolar Monolayer Domain : Perturbation Analysis

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電気四重極子密度と自発分極との相互作用がドメイン形状の形成に重要な寄与をすることを発見したことから、リン脂質のラセミ混合膜が液相-凝縮相の共存領域で形成するドメインの形状の形成原因を明らかにするために、単分子膜から発生する自発分極と電気四重極子密度を考慮に入れて、静電的なモデルを構築した。トルクバランス方程式と化学ポテンシャルの釣り合いの式から、ラセミ混合膜は、単分子膜の圧縮中に、ドメインの内部でキラル相分離を起こす可能性を見出した。

Monolayers form non-centrosymmetric orientational structure, and generate characteristic polarizational phenomena, e.g. spontaneous, linear, and second order non-linear polarizations. The orientational structure of monolayers is represented by the orientational order parameters $S_n (= \langle P_n(\cos \theta) \rangle)$. We have developed Maxwell displacement current (MDC), Brewster angle reflectometry / microscopy (BAR/BAM), and optical second harmonic generation (SHG) measurement techniques to measure S_1 , S_2 , and S_3 by probing the dielectric polarization generated from monolayers [1]. Monolayers form characteristic domain shape in the liquid-condensed two-phase coexistent states. Electrostatic energy is stored in monolayer domains with $S_1 \neq 0$ due to the generation of spontaneous polarization, and plays an important role in the formation of domain shape. Chiral dependence of dipalmitoyl-phosphatidylcholine (DPPC) monolayer domains has been observed by BAM [2]. In our previous study, we have constructed a model of phospholipid monolayer domains taking into account the electrostatic energy due to the spontaneous polarization and electric quadrupole density, and have clarified the mechanism of chiral dependence of monolayer domain shape focusing on the contribution of electric quadrupole density [3]. Recently, we have observed "wrench"-shaped domains from racemic DPPC monolayer, and it indicates that L- and D-DPPC molecules were phase separated in a domain [4]. In the present study, we extend our previous model to racemic domain to clarify the mechanism of chiral phase separation and of wrench-shape formation of racemic domains [4]. In this paper, we perform a perturbation analysis on the electrostatic energy, and demonstrate a possibility of chiral phase separation during a monolayer compression.

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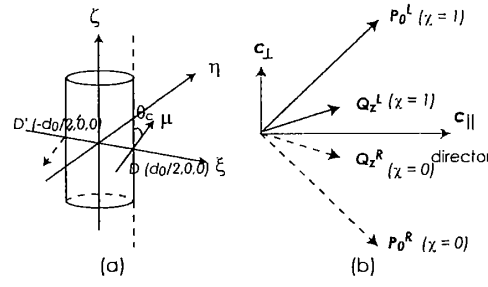


Figure 1: (a) The cylinder model of chiral phospholipid molecule. (b) Chiral dependence of orientational configuration of the in-plane spontaneous polarization and electric quadrupole density (topview).

Generation of electric quadrupole density is a characteristic of chiral molecules in our present molecular model (see Fig. 1). When monolayers establish in-plane orientational order, e.g. in condensed phase domain, the in-plane spontaneous polarization \mathbf{P}_\parallel and electric quadrupole density \mathbf{Q}_z are generated from such monolayers. The orientational configuration of \mathbf{P}_\parallel and \mathbf{Q}_z is dependent on the chirality of chiral monolayers. Assuming that the orientational distribution function is not dependent on the mixing ratio $\chi(\mathbf{R})$ of left-handed molecules to right-handed molecules as a function of points \mathbf{R} , \mathbf{P}_\parallel and \mathbf{Q}_z at \mathbf{R} in a racemic domain are expressed as $\mathbf{P}_{0\parallel} = P_0^{ach} \mathbf{c}_\parallel + 2(\chi - \frac{1}{2}) P_0^{ch} \mathbf{c}_\perp$ and $\mathbf{Q}_z = Q_z^{ach} \mathbf{c}_\parallel + 2(\chi - \frac{1}{2}) Q_z^{ch} \mathbf{c}_\perp$ (see Fig. 1 (b)). We derived the shape free energy of monolayers taking into account the surface pressure difference ΔP , the line tension λ , the electrostatic energy due to the normal and in-plane spontaneous polarization and electric quadrupole density, mixing entropy, and the chemical potential to keep the total mixing ratio a half. Calculating the variation in terms of the orientation of director \mathbf{c}_\parallel and χ , we further derived the torque balance equation and equation of chemical potential balance for circular domain. When $\chi = 1/2$, $\mathbf{c}_\parallel = \mathbf{a}_r$ is the only solution of the two equations (\mathbf{a}_r : unit vector to radial direction). We performed a perturbation analysis around this solution, and reduce the equation of chemical potential balance in the similar form to the corresponding equation of Bragg-Williams theory of phase separation. It suggests the possibility of chiral phase separation in a monolayer domain of racemic mixture.

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